Sol-Gel-Derived Oxide Thin Films Containing Metal Nanoparticles - Control and Application of Surface Plasma Resonance (SOLID STATE CHEMISTRY - Amorphous Materials)

AUTHOR(S):

Kozuka, Hiromitsu; Hashimoto, Tadanori; Uchino, Takashi; Yoko, Toshinobu

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Hiromitsu Kozuka, Tadanori Hashimoto, Takashi Uchino and Toshinobu Yoko

SiO_2 coating films containing Au nanoparticles were prepared by the sol-gel method. The size and shape of the dispersed Au particles, which determine the characteristics of the surface plasma resonance (SPR), could be varied in a wide range; the size could be varied from 4 to 40 nm, and the shape was spherical or elongated depending on the preparation conditions. Elongated Au nanoparticles of aspect ratios of 2 - 4 could be precipitated and aligned along the microscopically oriented pseudoboehmite particles, suggesting the possible production of the films with anisotropic SPR. TiO_2 film electrodes containing dispersed Au or Ag nanoparticles were prepared by the sol-gel method. Anodic photocurrents were observed in the visible region, resulting from the SPR-enhanced excitation of electrons from the surface states.

Keywords: Nanocomposites/ Coating films/ Sol-gel method/ Inorganic photonic materials/ Photoelectrodes

Nanocomposites composed of ultrafine metal particles and oxide matrices are now attracting much attention as advanced photonic materials. Surface plasma resonance (SPR) of metal particles, which enhances the oscillating electric field inside and outside nearby the particles, is the source of optical effects such as enhanced fluorescence and Raman scattering (SERS) of molecules, and enhanced optical third order nonlinearity. What is demanded for preparing materials of SPR-induced optical functions are to control the size and shape of the metal particles and to incorporate metal particles in high volume fraction; the former determines the wavelength of SPR and the latter provides intense SPR. Another challenging task is to align elongated metal particles in the matrices. Aligned, elongated metal particles exhibit anisotropic SPR, i.e., SPR that depends on the direction of oscillating electric field. Such materials with aligned texture can be used as polarizers in optical isolators.

For preparing composite materials containing metal nanoparticles in high volume concentration, the sol-gel method has many advantages, because undesired segregation of large metal particles, which easily occurs in solutions and glass melts, can be avoided in mesoporous gel matrices. In addition, the size and shape of the metal particles can be controlled through controlling the gel pore structure and

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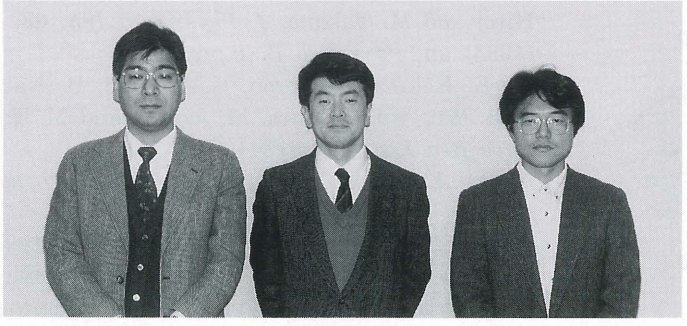
Scope of research

Inorganic amorphous materials with various functions are the targets of research in this laboratory. (1) To obtain a clear view of "what is glass" and the bases for designing functional glasses, we investigate the structure of glasses using X-ray and neutron diffraction analysis, high resolution MAS-NMR, and ab initio MO calculation. (2) To develop materials of high optical nonlinearity, we search heavy metal oxide-based glasses and transition metal oxide thin films, and evaluate the nonlinear optical properties by THG and Z-scan methods. (3) Using sol-gel method, synthesis and microstructure control are carried out on ceramic/metal/organic dye composite thin films.



YOKO KOZUKA UCHINO

Professor
YOKO, Toshinobu (D Eng)
Associate Professor
KOZUKA, Hiromitsu (D Eng)
Instructor
UCHINO, Takashi (D Eng)
Guest Research Associates
INNOCENZI, Plinio
Students
TERASHIMA, Kentaro (DC)
SAKAI, Hideo (MC)
SAKIDA, Shin-ichi (MC)
TAKAHASHI, Yasuhumi (MC)
NAKATA, Kunihiko (MC)
ONOGI, Takayuki (UG)
TOKUDA, Youmei (UG)
HATTORI, Takeshi (RS)

the gel matrix properties.

SiO_2 coating films containing Au nanoparticles of 1 - 3 % in volume fraction were prepared from hydrolyzed $Si(OC_2H5)_4$ solutions containing $HAuCl_4 \cdot 4H_2O$. The size of the Au particles could be varied from 4 to 40 nm, and the shape was spherical or elongated depending on the preparation conditions such as the sol aging time and the amount of H_2O for $Si(OC_2H_5)_4$ hydrolysis. Elongated Au nanoparticles could be precipitated in pseudoboehmite films and aligned along the microscopically oriented fibrous pseudoboehmite particles. TEM observation of the coating films revealed precipitation of aligned, elongated Au nanoparticles of aspect ratios of 2 - 4 (Fig. 1). The optical absorption due to SPR of Au particles, however, did not show any dependence on the direction of polarization, suggesting that the elongated Au particles are aligned only in a microscopic region. In order to achieve the macroscopically aligned texture, the dispersion state of the pseudoboehmite sol particles and the flow characteristics of the sol should be much more carefully controlled.

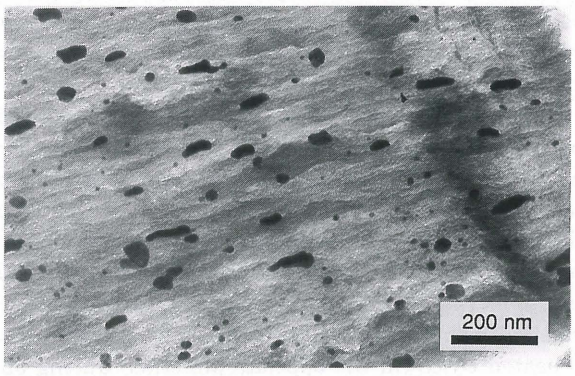


Figure 1. The TEM picture of a gel-derived pseudoboehmite coating film containing aligned, elongated Au nanoparticles.

Introduction of metal nanoparticles in photoelectrodes for solar cells is a possible innovative application of SPR. TiO_2 is believed to be one of the promising candidates for photoanode materials that split water due to its high chemical and photoelectrochemical durability. However, TiO_2 has low solar energy conversion efficiencies due to its large bandgap. Widely studied dye-sensitization extends the TiO_2 photoresponse to the visible region. In practice, however, the sensitizing quantum yield tends to be quite low, which is believed to be due to a fast back-reaction of the injected electrons. Enhancement of photochemical process of the sensitizers by SPR would be a possible way to increase the dye-sensitized quantum efficiency.

Firstly, the effect of Au and Ag nanoparticles on the photoelectrochemical properties of TiO_2 electrodes was investigated. TiO_2 film electrodes of 0.4 μm in thickness with a thin TiO_2 overlayer containing dispersed Au or Ag nanoparticles of 6 - 20 nm in size and 0.3 - 3 % in volume fraction were prepared by the sol-gel method. Anodic photocurrents were observed in the visible region for these electrodes (Fig. 2), which was thought to result from the SPR-enhanced excitation of electrons from the surface states. The introduction of larger amounts of the metal particles, however, reduced the anodic photocurrent in the UV region, resulting from the retardation of the electron transfer at the metal/TiO_2 Schottky barrier and by the TiO_2 band edge fluctuation.

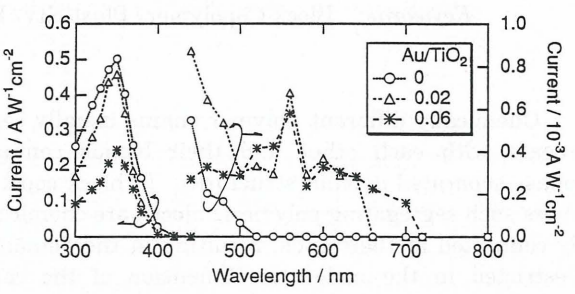


Figure 2. The action spectra of the TiO_2 film electrodes containing Au nanoparticles measured in a three electrodes system at a bias potential of 1 V vs. SCE.

Secondly, the effects of the incorporation of Au and Ag nanoparticles on the photoanodic properties were studied for rose bengal-deposited TiO_2 film electrodes. The dye-induced visible region photoresponse decreased with increasing Ag content, while the UV photoresponse increased. On the other hand, the dye-induced visible region photoresponse decreased to a less extent by incorporating Au particles, accompanied with the decrease in the UV photoresponse. Selection of metals, dyes and bias potentials and control of the separation between the metal particles and dye molecules would possibly improve the SPR-enhanced dye-sensitization.

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